

*The Charges on Ions in Gases, and Some Effects that Influence
the Motion of Negative Ions.*

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1. In two previous papers published in the 'Proceedings of the Royal Society,'* a method was described of finding directly the charges on positive and negative ions produced by secondary Röntgen rays in gases, in terms of the charge on a monovalent ion in a liquid electrolyte; and the results of some experiments made with air were given.

A number of investigations have since been made with oxygen, hydrogen, and carbonic acid, which have taken a considerable time to complete, for although a determination of the charge can be made very accurately from a few simple observations, it requires a long time to investigate the effect produced by complete drying on the motion of the negative ions. This effect can be observed by means of the same kind of experiments as are necessary for determining the charges on the ions, and it is of considerable interest to find at what forces and pressures the negative ions in dry gases assume the corpuscular state and move under an electric force according to laws that are quite different from those which govern the motions of the positive ions.

In all these experiments exactly similar results were obtained with the three gases that have been examined, as were previously obtained with air.

With regard to the charges on the negative ions, the values obtained for the product Ne (N being the number of molecules per cubic centimetre in a gas at 760 mm. pressure and 16° C., and e the charge on an ion in electrostatic units) with different forces, pressures, and strengths of radiation were all practically the same and nearly equal to 1.22×10^{10} , which is the value of Ne for monovalent ions in liquid electrolytes. The mean values of Ne obtained in a set of experiments were 1.23×10^{10} , 1.24×10^{10} , 1.23×10^{10} , for oxygen, hydrogen, and carbonic acid respectively.

The values of Ne for positive ions, under different conditions of force and pressure, were nearly the same as for negative ions when the secondary rays ionising the gas proceed from a bright metallic surface, the corresponding numbers being 1.24×10^{10} , 1.26×10^{10} , and 1.32×10^{10} . Higher values of Ne were obtained for positive ions in all gases when the rays proceeded from a surface covered with a thin layer of vaseline, showing that some of the positive ions produced by the more penetrating radiation have double

* 1908, A, vols. 80 and 81.

charges. The mean values obtained for the three gases under these conditions are 1.71×10^{10} , 1.84×10^{10} , and 1.55×10^{10} .

2. The principle that was used in these investigations was to allow a stream of ions to pass through a circular aperture in a thin plate, and after passing along a certain distance under the action of a known electric force X , to receive the ions on a disc of the same diameter as the aperture and on a flat ring surrounding the disc. The stream opens out as the ions move under the electric force, and according to the ordinary laws of diffusion the ratio R of the charge received by the disc to that received by the surrounding ring depends only on the product NeX . There is therefore a definite relation between R and X which is independent of the pressure when the motion of the ions obeys the simple laws of diffusion, as is always the case with the positive ions with the pressures and forces used in these experiments; so that the value of Ne can easily be obtained.

In finding the values of Ne for negative ions it is convenient to have a slight amount of water vapour in the gas (1/10th of a millimetre pressure is sufficient when dealing with oxygen at 10 mm. pressure, or with hydrogen at 30 mm. pressure), as the negative ions then obey the simple laws of diffusion under which their kinetic energy of agitation (or the partial pressure of the ions) is equal to that of an equal number of molecules of the gas in which they move. The determinations of Ne may also be made in perfectly dry gases at somewhat higher pressures when forces not exceeding 1 volt per centimetre are used.

3. When a gas has been dried for several days and the pressure is below a certain value, depending on X/P , a large increase in the lateral diffusion of the stream of negative ions is obtained, and only a small proportion of the ions is received on the disc on which the centre of the stream impinges. With a given force, the pressure at which this effect can be observed is greater in hydrogen than in oxygen, and is much smaller in carbonic acid than in the other gases. When this stage is arrived at the ratio R no longer follows the ordinary laws of diffusion. If the force is kept constant the opening out of the stream increases rapidly (R diminishes) as the pressure of the gas is diminished, which is in marked contrast to the effects obtained when a little water vapour is present, as the value of R is then independent of the pressure of the gas P . Thus, in dry oxygen, with a force of 2 volts per centimetre, the ratio of the charges R was found to be 0.465 when the pressure was 10 mm., and 0.27 when the pressure was 5 mm.; whereas, if a small amount of water vapour were present, both these ratios would be about 0.57.

As has already been mentioned in one of the previous papers, the motion

of the negative ions in a dry gas at low pressure can be explained on the supposition that the negative ions have assumed the corpuscular state when the value of X/P is sufficiently great, and the relative high velocity in directions perpendicular to the direction of the electric force is due to an increase of the velocity of agitation above the average value this velocity would assume if the ions were in thermal equilibrium with the molecules of the gas.

From the experiments which have been made, it is easy to deduce the ratio of the partial pressure of the ions when diffusing in this way to the partial pressure of an equal number of molecules in thermal equilibrium with the gas, and the curves obtained for air show that when $X = 1$ volt per centimetre and $P = 10$ mm., the partial pressure of the ions is twice that of an equal number of molecules.* Since the partial pressure is proportional to mv^2 , this result shows that the velocity of agitation v of the ions is greater by the factor $\sqrt{2}$ than the velocity of agitation of particles of the same mass in thermal equilibrium with the molecules of the gas.

The conclusion to which these experiments lead indicates that the velocities due to electric forces of negative ions in dry gases should be very large when the values of X/P are of the same order as those used in the above experiments.

4. Mr. R. T. Lattey† has recently investigated the velocities under these conditions, and he has found that in dry air large increases in the velocity of negative ions are obtained by making comparatively small increases in the electric force. Thus, in air at 10 mm. pressure, the velocity due to a force of 0.5 volt per centimetre is 173 cm. per second, and when the force is increased to 0.9 volt per centimetre, the velocity is 1845 cm. per second.

It is interesting to apply the theory of diffusion to calculate the coefficient of diffusion of negative ions into air under the above conditions, as the investigation shows how the group of molecules associated with each ion diminishes as the force increases. This method was used some time ago‡ to find the masses of negative ions in gases at atmospheric pressure when acted on by small forces. When X/P is small, then, the apparent mass of an ion in air is constant over a large range of values of X/P . The rate of diffusion of the ions is slow in this case, and, by comparing the rate of diffusion of ions into air with that of CO_2 into air, it may be seen that the apparent mass of the ion is about 11 times as great as that of a molecule of carbonic acid.

In applying the theory of diffusion to the cases in which X/P is large, it is

* J. S. Townsend, 'Roy. Soc. Proc.,' 1908, vol. 81, p. 468.

† R. T. Lattey, 'Roy. Soc. Proc.,' 1910, A, vol. 84.

‡ J. S. Townsend, 'Phil. Trans.,' 1899, A, vol. 193.

necessary to give the correct value to the partial pressure p of the ions, since the velocity under the electric force and the rate of diffusion both depend on the velocity of agitation of the ions.

The equations of motion of the ions are of the form

$$\frac{1}{K}(pu) = -\frac{dp}{dx} + nXe,$$

so that the velocity u under the force X is given by the equation

$$\frac{1}{K}(pu) = nXe,$$

K being the coefficient of diffusion while the force is acting.

Usually, as when X/P is small, the partial pressure p of the ions is connected with the number of ions per c.c., n , by the equation $p/n = \Pi/N$, N being the number of molecules per cubic centimetre of a gas at atmospheric pressure Π and temperature 16°C ., which is the temperature of the gas when the velocity u was determined. When $X = 0.9$ volt per centimetre and $P = 10$ mm., the partial pressure p is larger than the above value by the factor 1.85, so that on substituting for p its value in terms of n the equation for K becomes

$$K = \frac{1.85 \times \Pi u}{NeX} = 93,$$

since $u = 1845$, $X = 0.9/300$ and $Ne = 1.22 \times 10^{10}$.

The high value thus obtained for K is due partly to the fact that the velocity of agitation of the ions exceeds that of particles of equal mass in thermal equilibrium with the gas by the factor $\sqrt{1.85}$. Hence particles of* equal mass would, under ordinary conditions, diffuse into air at 10 cm. pressure at a rate corresponding to the value of K , $93/\sqrt{1.85} = 71$. The coefficient of diffusion of CO_2 into air is 1.42, the sum of the pressures of the gases being 760 mm., so that at 10 cm. pressure the coefficient of interdiffusion would be 10.8. Experiments on diffusion show that the coefficients of interdiffusion are inversely proportional to $\sqrt{m_1 m_2}$, m_1 and m_2 being the masses of the molecules of the two gases. Hence the ratio of the mass M of the negative ion to the mass m of a molecule of CO_2 is $M/m = (10.8)^2/(71)^2 = 1/43$. The quantity M is the average value of the mass of the group of molecules associated with the ion, which is continually changing, and the above investigation shows that the average value must be less than the mass of a molecule of air when $X/P = 0.09$. This shows that during part of the

* Since the rates of diffusion of different gases into a standard gas are approximately proportional to the velocities of agitation of the molecules of the different gases, it is assumed here that the rates of diffusion of the ions are also proportional to their velocities of agitation.

time the negative electron must be free from molecules of the gas. When X/P increases, M becomes smaller still, but as the velocities have not yet been determined accurately for higher values of X/P , further investigation on these lines must be postponed.

In order that the equations of diffusion should hold in these cases, it is necessary that the velocity of the ion in the direction of the electromotive force should be small compared with the velocity of agitation. It is easy to show that this condition holds. Since the velocity of agitation of a molecule of CO_2 at 0° centigrade is 4×10^4 centimetres per second, the velocity of particles of an average mass $1/43$ of that of the molecules of CO_2 would be 2.8×10^5 , and while under the electric force their velocity of agitation would be $2.8 \times 10^5 \times \sqrt{1.85} = 3.8 \times 10^5$, which is large compared with the velocity, 1845 centimetres per second, in the direction of the electric force.

On the Energy and Distribution of Scattered Röntgen Radiation.

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Introduction.

It has been shown by Prof. Sir J. J. Thomson that it is possible, on certain assumptions, to calculate the number of electrons in an atom of any element from considerations of the scattering undergone by a rapidly moving electrified particle in the substance. In a paper recently read before this Society* I was able, by means of experiments there described, to show that the scattering of homogeneous β -rays by thin sheets of different substances did follow very closely the laws predicted by the theory, and to calculate the number of electrons contained in the atoms of some half dozen different elements. It was found that, in every case, the number of electrons per atom was equal to about three times the atomic weight.

Although the agreement between theory and experiment was very close, it seemed desirable to collect as much independent evidence as possible upon such a point. Some years ago Prof. Sir J. J. Thomson† showed that in the phenomenon of the scattering of a beam of Röntgen rays we have another possible method of attacking the problem.

* 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 226.

† 'Conduction through Gases,' 1906, p. 321.